



Solvent-free aerobic alcohol oxidation using Cu/Nb₂O₅: Green and highly selective photocatalytic system

Shinya Furukawa, Ayaka Tamura, Tetsuya Shishido*, Kentaro Teramura, Tsunehiro Tanaka**

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto Daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

ARTICLE INFO

Article history:

Received 27 June 2011

Received in revised form 22 August 2011

Accepted 7 September 2011

Available online 14 September 2011

Keywords:

Alcohol oxidation

Niobium oxide

Photocatalyst

Selective oxidation

Solvent-free

ABSTRACT

Photooxidation of alcohols without organic solvents in the presence of O₂ took place at the atmospheric pressure and room temperature over Nb₂O₅ and Cu/Nb₂O₅, avoiding the cost, toxicity, and purification problems associated with transition-metal systems. Loading of a small amount of copper on Nb₂O₅ significantly enhanced activity without lowering selectivity. On the other hand, loading of Pt, Ni, Rh, Ru, and Ag showed no promotion effect. The selectivities of the photooxidation of aliphatic, aromatic and heteroatom-containing alcohols over Cu/Nb₂O₅ were in the range of 80–99%. Cu/Nb₂O₅ was easily separated from the reaction mixture and was reusable without reducing the catalytic performance.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Alcohol oxidation to corresponding carbonyl compounds is one of the most useful and the simplest transformations in organic and industrial chemistry. Non-catalytic methods with stoichiometric, toxic, corrosive and expensive oxidants such as ClO[−], dichromate, permanganate, and peroxy acids under stringent conditions of high pressure and/or temperature have been widely used for alcohol oxidations [1–4]. In addition, these reactions are often carried out with high concentration of bases and environmentally unfriendly organic solvents. Therefore, much attention has been paid to the development of heterogeneous catalytic systems that use clean and atom efficient oxidants like molecular oxygen or H₂O₂ without organic solvents [5–16]. Therefore, the development of catalytic systems for alcohol oxidation has been one of the most pursued targets in last decade, due to substituting them with heterogeneous catalytic oxidation using clean and atom-efficient oxidants such as molecular oxygen without organic solvents.

Recently, the aerobic alcohol oxidation was successfully carried out by using heterogeneous catalysts such as tetrapropylammonium perruthenate (TPAP)/MCM-41 [8], Ru/CeO₂ [9], Ru-hydroxalcalite [10], Ru/hydroxyapatite (Ru-HAP) [11,12], [RuCl₂(*p*-cymene)]/activated carbon [13], Ru/Al₂O₃ [14], and Pd-hydroxalcalite

which requires the addition of pyridine [15], and Pt on activated carbon [16]. These systems require the use of organic solvents like toluene and trifluorotoluene. Solvent-free aerobic oxidation of alcohols by Pd/Al₂O₃ was also reported [17], however, the use of the noble metal Pd is essentially required.

In this respect, photoreactions are promising processes and the development of photocatalysts is a subject that is now receiving noticeable attention. TiO₂ has been identified as one example of a practical and useful photocatalysts [18–22], and widely used in degradation of organic pollutants in air and water. In the most part of these reports, TiO₂ is used in vapor phase oxidations at high temperatures [18], oxidation of only lower alcohols [19–21], oxidation using solvents such as benzene [22] and a low selectivity to partial oxidized products due to excess photo-activation of target products which leads to deep oxidation. Zhao et al. [23,24] reported that the photooxidation of alcohols on TiO₂ could be dramatically accelerated without any loss of selectivity by adsorption of Brønsted acid and this effect by Brønsted acid results from the decomposition of the relatively stable side-on peroxide promoted by the protons, which effectively clean the catalytic Ti–OH₂ sites. Recently, Su and co-workers reported that mesoporous graphite carbon nitride (mpg-C₃N₄) can work as effective photocatalyst for the selective oxidations of benzylic alcohols with visible light. However, these systems require the use of benzotrifluoride as a solvent.

Here, we report that Nb₂O₅ and Cu/Nb₂O₅ catalyze photooxidation of various aliphatic and aromatic alcohols without solvents in the presence of O₂ at the atmospheric pressure and room temperature. We found that loading of a small amount of copper on Nb₂O₅ significantly enhanced activity without lowering

* Corresponding author. Tel.: +81 075 383 2559; fax: +81 075 383 2561.

** Corresponding author. Tel.: +81 075 383 2558; fax: +81 075 383 2561.

E-mail addresses: shishido@moleng.kyoto-u.ac.jp (T. Shishido),

tanakat@molemg.kyoto-u.ac.jp (T. Tanaka).

selectivity, whereas loading of Pt, Ni, Rh, Ru, and Ag showed no promotion effect. This strongly suggests that the role of Cu on Nb₂O₅ is different from those of precious metals such as Pt and Rh on TiO₂ photocatalyst, in other words, the promotion of charge separation.

2. Experimental

2.1. Preparation

Niobic acid, niobium oxide hydrate (Nb₂O₅·*n*H₂O, AD/2872, HY-340) was kindly supplied from CBMM. Other chemicals used were of reagent grade and were obtained from Aldrich Chemical Co., Tokyo Kasei Kogyo Co., Ltd. and Wako Pure Chemical Industries, Ltd. All reagents were used without further purification.

Niobium oxide (Nb₂O₅) catalyst was prepared by calcination of niobic acid in a dry air flow at 773 K for 5 h (BET surface area: 48 m² g^{−1}). A series of niobium oxide supported metal catalysts (M/Nb₂O₅; M = Ru, Rh, Ni, Pt, Cu, and Ag) was prepared by impregnation of niobic acid with an aqueous solutions of metal salts (RuCl₃, RhCl₃, Ni(NO₃)₂, H₂PtCl₄, Cu(NO₃)₂ and Ag(NO₃)) at 353 K, followed by evaporation, drying and calcination at 773 K in a stream of dry air for 5 h. After calcination, the catalysts were ground into powder under 100 mesh (0.15 mm). M/Nb₂O₅ catalysts were reduced under 5% H₂/N₂ flow at 20 cm³ min^{−1} for 0.5 h at 673 K prior to use.

2.2. Characterization

BET surface areas of catalysts were determined using N₂ adsorption isotherm at 77 K measured by a BELSORP 28SA (BEL Japan Corp.). Crystal phase of each catalyst was determined by X-ray diffraction technique (XRD) under ambient conditions at room temperature using a Shimadzu XD-D1 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å).

2.3. Photooxidation of alcohols

The photocatalytic oxidation of alcohol was carried out in a quasi-flowing batch system (see Supporting Information, Fig. S1). Catalyst (100 mg) and a stirring bar were introduced to the Pyrex glass reactor (cut-off light below 300 nm). An alcohol as a substrate (10 ml) without solvent was introduced into the reactor. The suspension was vigorously stirred at room temperature and irradiated from the flat bottom of the reactor through a reflection by a cold mirror with a 500 W ultra-high-pressure Hg lamp (USHIO Denki Co.). Oxygen was flowed into the reactor at 2 cm³ min^{−1} (0.1 MPa). At the down stream of the flow reactor, a saturated barium hydroxide solution (Ba(OH)₂) was equipped to determine the quantity of carbon dioxide (CO₂) as barium carbonate (BaCO₃). Products were analyzed and quantified by FID-GC (Shimadzu GC14B) and GC-MS (Shimadzu QP-5050).

3. Results and discussion

3.1. Solvent-free photooxidation of 1-pentanol over M/Nb₂O₅

Table 1 shows the results of photooxidation of 1-pentanol over Nb₂O₅ and M/Nb₂O₅ (M = Ru, Rh, Ni, Pt, Cu, and Ag) with molecular oxygen under irradiation at 323 K. The photogenerated products were pentanal (RCHO) as a main product, and a small amount of pentanoic acid (RCOOH) and carbon dioxide (CO₂). Control experiments revealed that catalyst, oxygen and photo irradiation are necessary for the reaction (entries 12–14). The evolution of photogenerated products occurred in response to illumination. These results indicate that photooxidation of 1-pentanol over Nb₂O₅ and M/Nb₂O₅ was due entirely to a photocatalytic reaction. We have

Table 1

Photocatalytic activities of M/Nb₂O₅ (M = Ru, Rh, Ni, Pt, Cu, and Ag) in solvent-free photooxidation of 1-pentanol.^a

Entry	Catalyst	Loading (mol%)	Yield (μmol) ^b
1	Nb ₂ O ₅	–	355
2	Ru/Nb ₂ O ₅	2.6	315
3	Rh/Nb ₂ O ₅	2.6	305
4	Ni/Nb ₂ O ₅	2.6	220
5	Pt/Nb ₂ O ₅	2.6	340
6	Ag/Nb ₂ O ₅	2.6	445
7	Cu/Nb ₂ O ₅	0.65	780
8	Cu/Nb ₂ O ₅	1.3	1145
9	Cu/Nb ₂ O ₅	1.9	1285
10	Cu/Nb ₂ O ₅	2.6	1125
11	Cu/Nb ₂ O ₅	5.2	880
12 ^c	Cu/Nb ₂ O ₅	1.9	36
13 ^d	Cu/Nb ₂ O ₅	1.9	n.d.
14	None	–	n.d.

^a Reaction condition: catalyst (100 mg), 1-pentanol (10 ml), oxygen flow (2 cm³ min^{−1}), λ > 300 nm, irradiation time, 5 h.

^b Amount of pentanal produced.

^c Under 1 atm N₂.

^d In the dark.

already reported that Nb₂O₅ shows higher selectivity to pentanal than TiO₂ at the same conversion level although TiO₂ shows higher activity than Nb₂O₅ [25]. Cu/Nb₂O₅ showed much higher activity than that of bare Nb₂O₅ (entries 1 and 7–11). On the other hand, when Ru, Rh, Ni, Pt, and Ag were supported on Nb₂O₅, the yields were almost similar to or slightly lower than that of bare Nb₂O₅ (entries 1–6). XRD patterns of Nb₂O₅ and M/Nb₂O₅ showed diffraction lines assignable to TT-phase Nb₂O₅ with a pseudohexagonal structure (Fig. 1). No diffraction line due to these metal species was detected, indicating that these metal species were highly dispersed or with amorphous. It has been reported that modification with a small amount of highly dispersed metal species like Pt [20,22,26], Rh [27] and Ni [28] improves the photocatalytic activity of TiO₂. Usually, it is thought that these metal species supported on TiO₂ act as an electron acceptor, resulting in inhibiting the recombination of photoactivated electrons and positive holes (charge separation mechanism). Therefore, above results of photooxidation over Nb₂O₅ and M/Nb₂O₅ suggest that the role of Cu supported on Nb₂O₅ is different from that of metal species on TiO₂, i.e., electron acceptor in charge separation mechanism. Hashimoto and co-workers reported that Cu(II) species grafted on TiO₂ promotes the oxidative decomposition of 2-propanol even under visible light (>450 nm) irradiation [29,30]. They also proposed that visible light initiates interfacial charge transfer (IFCT)

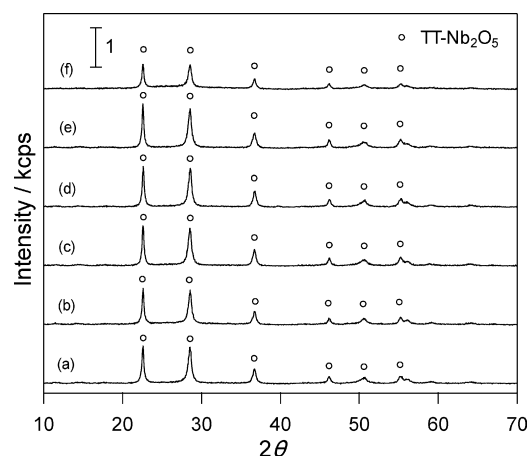


Fig. 1. XRD patterns of M/Nb₂O₅: M = (a) Ru, (b) Rh, (c) Ni, (d) Pt, (e) Cu and (f) Ag.

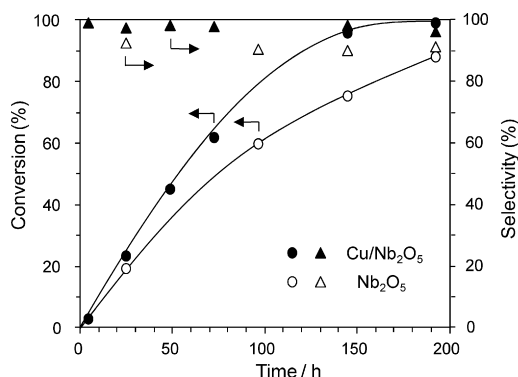


Fig. 2. Time course of conversions and selectivities in photooxidation of 1-phenylethanol over Cu/Nb₂O₅ and Nb₂O₅. Filled circle and triangle are the conversion and selectivity over Cu/Nb₂O₅ and unfilled circle and triangle are those over Nb₂O₅.

[31–33], in other words, electron in the valence band of TiO₂ are directly transferred to Cu(II) and form Cu(I). In the IFCT mechanism, Cu(II) acts as an electron acceptor. Recently, we found that the photooxidation of 1-pentanol over Nb₂O₅ took place under visible light irradiation up to 480 nm, although the band gap of Nb₂O₅ is 390 nm (3.2 eV) [34,35]. This observation indicates that the photo-activation mechanism of alcohol over Nb₂O₅ is different from the classical electron transfer mechanism found in semiconductor photocatalysis (the formation of an excited electron in the conduction band and the positive hole in the valence band). By means of UV–Vis, ESR, FT/IR with the aid of DFT calculations, the detailed reaction mechanism of photooxidation of alcohol over revealed and unique photo-activation mechanism by “*in situ doping*” (the direct electron transfer from the O 2p orbital derived from adsorbed alcoholate species to the conduction band consisting of Nb 4d orbitals) was proposed [34–37]. Moreover, kinetic analysis revealed that the rate-determining step of the photooxidation of alcohol over Nb₂O₅ is desorption of products. These results suggest that copper on Nb₂O₅ acts as an accelerator of the product desorption in addition to the promotor of charge separation. The detailed reaction mechanism and the role of copper of Cu/Nb₂O₅ are now under investigation and will be reported in the near future [36,37].

3.2. Photooxidation of alcohols over Cu/Nb₂O₅

The catalytic activities and selectivities for the solvent-free photooxidation of several aliphatic and aromatic alcohols over Nb₂O₅ and Cu/Nb₂O₅ with molecular oxygen at atmospheric pressure are summarized in Table 2 (entries 1–6). These aliphatic and aromatic alcohols were selectively oxidized to corresponding carbonyl compounds. The selectivity to cyclohexanone was slightly low (entry 4) among aliphatic alcohols tested. This may be due to autooxidation by the formation of radical species by the photo-activation (Norish Type I reaction) [38,39] of the produced cyclohexanone. In the case of aliphatic primary and secondary alcohols except for cyclohexanol (entry 4), the catalytic activities were significantly increased by loading of Cu. The conversions and selectivities in oxidation of aromatic alcohols were higher than those of aliphatic alcohols (entries 5 and 6). This tendency is similar to the conventional thermal catalyst. Primary alcohols were easier to be oxidized than secondary ones in the case of both of aliphatic and aromatic ones. This result is in contrast to the photooxidation of alcohol over TiO₂ film [18].

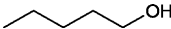
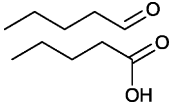
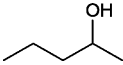
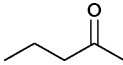
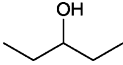
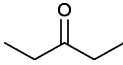
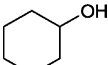
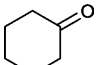
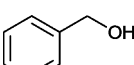
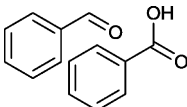
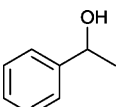
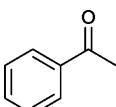
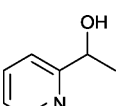
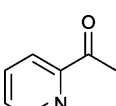
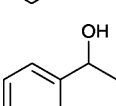
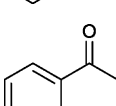
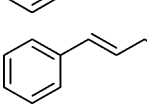
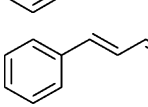
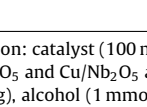
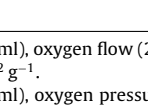
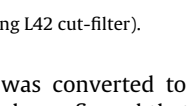
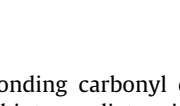
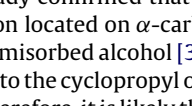
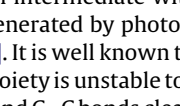
Fig. 2 shows the time course of photooxidation of 1-phenylethanol over Nb₂O₅ and Cu/Nb₂O₅. The conversion increased with irradiation time. On the other hand, the selectivity to acetophenone was almost constant. The formation rate of

acetophenone over Cu/Nb₂O₅ was higher than that of Nb₂O₅. Furthermore, in the case of Cu/Nb₂O₅, 1-phenylethanol was almost stoichiometrically oxidized after 192 h of photo irradiation even under solvent-free condition (96% yield; entry 6). Up to now, attempts to use photocatalyst for selective solvent-free aerobic oxidation of alcohols have met with very limited success. Fukuzumi et al. reported that 9-phenyl-10-methylacridium acts as an effective photocatalyst for solvent-free selective photocatalytic oxidation of benzyl alcohol under visible light irradiation via efficient photoinduced electron transfer from benzyl alcohol to the singlet excited state of the acridium ion [40]. However, turnover number (TON) of their system is quite small. To the best of our knowledge, our system (Cu/Nb₂O₅) is the first example that aerobic photooxidation of alcohol proceeded quantitatively even under solvent-free condition.

Leaching of active metal species into solution is important point to consider the stability of catalyst. After 5 h of photooxidation of 1-pentanol, Cu/Nb₂O₅ catalysts could be easily separated by filtration. Further irradiation to the solid-free solution did not give any products. Moreover, the separated Cu/Nb₂O₅ was successfully reused with no reduction in the activity and selectivity (see Supporting Information, Fig. S2) as well as the separated Nb₂O₅. These results strongly suggest that the photooxidation takes place on the surface of the Cu/Nb₂O₅ catalyst.

In the cases of photooxidations of α -methyl-2-pyridine methanol, α -cyclopropylbenzyl alcohol, and cinnamyl alcohol, benzene was used as a solvent (Table 1, entries 7–9). In the case of Pd catalysts, alcohols having heteroatom, such as (3-pyridyl)methanol, (2-aminophenyl)methanol and (3-thiophenyl)methanol did not proceed due to the complexation of Pd with the heteroatom [15]. However, by using Cu/Nb₂O₅, α -methyl-2-pyridine methanol was converted to the corresponding ketone in high yield. On the other hand, the photooxidations of α -cyclopropylbenzyl alcohol, and cinnamyl alcohol did not give the corresponding ketone and α,β -unsaturated aldehyde in high yields. In these cases, benzaldehyde was mainly produced as by-product, indicating that C–C or C=C bond was cleaved at α -position in each case. Interestingly, the selectivities to corresponding ketone and α,β -unsaturated aldehyde moderately increased by the addition of Cu to Nb₂O₅. To confirm the contribution of photoreaction of α -cyclopropylbenzyl alcohol and cinnamyl alcohol, these alcohols were irradiated in the absence of catalyst. The conversions of α -cyclopropylbenzyl alcohol and cinnamyl alcohol were 71 and 99% after 48 h of irradiation, respectively. This result indicates that a part of benzaldehyde formation was due to the photoreaction of these alcohols independently of the photo-activation by photocatalyst. On the other hand, the photoreaction of these alcohols in the absence of catalyst did not take place under visible light irradiation (>390 nm). The photooxidation of these alcohols with Nb₂O₅ or Cu/Nb₂O₅ catalysts were tested under visible light irradiation. Although the band gap of Nb₂O₅ is 390 nm, the photooxidations proceeded over Nb₂O₅ and Cu/Nb₂O₅, and the selectivities to corresponding ketone and α,β -unsaturated aldehyde improved (entries 8b and 9b). Moreover, Cu/Nb₂O₅ showed higher selectivities than those over Nb₂O₅. However, these selectivities are not still sufficiently high and admit of improvement. In our previous work, we proposed unique photo-activation mechanism by “*in situ doping*” (the direct electron transfer from the electron donor level derived from adsorbed alcoholate species to the conduction band of photocatalyst) [34,35]. The fact that the photooxidation of α -cyclopropylbenzyl alcohol and cinnamyl alcohol proceeded even under visible light irradiation supports that the photooxidation of alcohols over Nb₂O₅ and Cu/Nb₂O₅ took place by this “*in situ doping*” mechanism. In our proposed mechanism, the radical species was formed by the direct electron transfer from the electron donor level to the conduction band under photo-irradiation, and then

Table 2
Photooxidations of various alcohols catalyzed by Cu/Nb₂O₅ and Nb₂O₅.^a

Entry	Substrate	Products	Time (h)	Cu/Nb ₂ O ₅		Nb ₂ O ₅	
				C (%)	S (%)	C (%)	S (%)
1			48	33	80	16	71
2			48	26	86	12	87
3			48	23	82	8	93
4			48	30	81	37	81
5			24	36	99	37	99
6			24	24	98	19	93
			192	99	96	88	92
7 ^b			48	94	91	93	90
8a ^b			48	97	59	99	50
8b ^{b,c}			48	40	64	42	61
9a ^b			48	96	21	99	11
9b ^{b,c}			48	51	49	76	30

^a Reaction condition: catalyst (100 mg), alcohol (10 ml), oxygen flow (2 cm³ min⁻¹), $h\nu > 300$ nm; C: conversion of alcohol; S: selectivity to partial oxidation products. BET surface areas of Nb₂O₅ and Cu/Nb₂O₅ are 48 and 59 m² g⁻¹.

^b Catalyst (100 mg), alcohol (1 mmol), benzene (10 ml), oxygen pressure (0.1 MPa), $h\nu > 300$ nm. To avoid solvent evaporation, the oxidation was carried out in a closed system.

^c $h\nu > 390$ nm (using L42 cut-filter).

radical species was converted to corresponding carbonyl compound. We already confirmed that a radical intermediate with an unpaired electron located on α -carbon is generated by photoexcitation of the chemisorbed alcohol [34,36,37]. It is well known that a radical adjacent to the cyclopropyl or allyl moiety is unstable to easily rearrange. Therefore, it is likely that C–C and C=C bonds cleavage accompanied with the radical rearrangement occurs in the cases of photooxidation of α -cyclopropylbenzyl alcohol and cinnamyl alcohol. This undesired radical rearrangement probably results in the decrease of the selectivity to the desired product.

4. Conclusions

Solvent-free aerobic photooxidations of various alcohols over Cu/Nb₂O₅ and Nb₂O₅ were examined. Several alcohols were selectively oxidized into corresponding carbonyl compounds at room temperature under atmospheric pressure. The photocatalytic activities were remarkably enhanced by the addition of a small amount of Cu to Nb₂O₅ without lowering selectivities. 1-Pentylethanol was quantitatively oxidized to acetophenone by using Cu/Nb₂O₅ even

under solvent-free condition. A heteroatom-containing alcohol, α -methyl-2-pyridine methanol was selectively oxidized by using Cu/Nb₂O₅ and Nb₂O₅. On the other hand, Nb₂O₅ and Cu/Nb₂O₅ gave moderate selectivities in the photooxidation of an allylic alcohol (cinnamyl alcohol) or α -cyclopropylbenzyl alcohol. By the addition of a small amount of Cu to Nb₂O₅, the selectivities to the corresponding carbonyl compounds improved. Cu/Nb₂O₅ was easily separated from the reaction mixture and was reusable without reducing the catalytic performance.

Acknowledgements

This work was partially supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 17034036, “Molecular Nano Dynamics” and No. 20037038, “Chemistry of Concerto Catalysis”) and Scientific Research (No. 19360365, “B”) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. KT is supported by the Program for Improvement of Research Environment for Young Researchers from Special Coordination Funds for Promoting Science and Technology (SCF) commissioned by the

Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. S. Furukawa thanks the JSPS Research Fellowships for Young Scientists.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2011.09.003.

References

- [1] R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- [2] M. Hudlicky, *Oxidations in Organic Chemistry*, American Chemical Society, Washington, DC, 1990.
- [3] C.L. Hill, *Advance in Oxygenated Process*, JAI, London, 1998.
- [4] R.C. Larock, *Comprehensive Organic Transformations*, VCH, New York, 1989.
- [5] R.A. Sheldon, I.W.C.E. Arends, A. Dijkman, *Catal. Today* 57 (2000) 157–166.
- [6] T. Mallat, A. Baiker, *Chem. Rev.* 104 (2004) 3037–3058.
- [7] N. Srinivas, V.R. Rani, M.R. Kishan, S.J. Kulkarni, K.V. Raghavan, *J. Mol. Catal. A: Chem.* 172 (2001) 187–191.
- [8] A. Bleloch, B.F.G. Johnson, S.V. Ley, A.J. Price, D.S. Shephard, A.W. Thomas, *Chem. Commun.* 190 (1999) 7–1908.
- [9] F. Vocanson, Y.P. Guo, J.L. Namy, H.B. Kagan, *Synth. Commun.* 28 (1998) 2577–2582.
- [10] T. Matsushita, K. Ebitani, K. Kaneda, *Chem. Commun.* 26 (1999) 5–266.
- [11] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 122 (2000) 7144–7145.
- [12] K. Mori, S. Kanai, T. Hara, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, *Chem. Mater.* 19 (2007) 1249–1256.
- [13] E. Choi, C. Lee, Y. Na, S. Chang, *Org. Lett.* 4 (2002) 2369–2371.
- [14] K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* 41 (2002) 4538–4542.
- [15] N. Kakiuchi, Y. Maeda, T. Nishimura, S. Uemura, *J. Org. Chem.* 66 (2001) 6620–6625.
- [16] T. Mallat, A. Baiker, *Catal. Today* 19 (1994) 247–283.
- [17] H.L. Wu, Q.H. Zhang, Y. Wang, *Adv. Synth. Catal.* 347 (2005) 1356–1360.
- [18] U.R. Pillai, E. Sahle-Demessie, *J. Catal.* 211 (2002) 434–444.
- [19] D.S. Muggli, J.T. McCue, J.L. Falconer, *J. Catal.* 173 (1998) 470–483.
- [20] J.L. Falconer, K.A. Magrini-Bair, *J. Catal.* 179 (1998) 171–178.
- [21] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, *Water Res.* 33 (1999) 661–668.
- [22] F.H. Hussein, G. Pattenden, R. Rudham, J.J. Russell, *Tetrahedron Lett.* 25 (1984) 3363–3364.
- [23] M. Zhang, Q. Wang, C.C. Chen, L. Zang, W.H. Ma, J.C. Zhao, *Angew. Chem. Int. Ed.* 48 (2009) 6081–6084.
- [24] Q. Wang, M. Zhang, C. Chen, W. Ma, J. Zhao, *Angew. Chem. Int. Ed.* 49 (2010) 7976–7979.
- [25] T. Ohuchi, T. Miyatake, Y. Hitomi, T. Tanaka, *Catal. Today* 120 (2007) 233–239.
- [26] M.D. Driessen, V.H. Grassian, *J. Phys. Chem. B* 102 (1998) 1418–1423.
- [27] Y. Kohno, H. Hayashi, S. Takenaka, T. Tanaka, T. Funabiki, S. Yoshida, *J. Photochem. Photobiol. A* 126 (1999) 117–123.
- [28] L.T. Prahov, J. Disdier, J.M. Herrmann, P. Pichat, *Int. J. Hydrogen Energy* 9 (1984) 397–403.
- [29] H. Irie, S. Miura, K. Kamiya, K. Hashimoto, *Chem. Phys. Lett.* 457 (2008) 202–205.
- [30] H. Irie, K. Kamiya, T. Shibamura, S. Miura, D.A. Tryk, T. Yokoyama, K. Hashimoto, *J. Phys. Chem. C* 113 (2009) 10761–10766.
- [31] C. Creutz, B.S. Brunschwig, N. Sutin, *J. Phys. Chem. B* 109 (2005) 10251–10260.
- [32] C. Creutz, B.S. Brunschwig, N. Sutin, *J. Phys. Chem. B* 110 (2006) 25181–25190.
- [33] R. Nakamura, A. Okamoto, H. Osawa, H. Irie, K. Hashimoto, *J. Am. Chem. Soc.* 129 (2007) 9596–9597.
- [34] T. Shishido, T. Miyatake, K. Teramura, Y. Hitomi, H. Yamashita, T. Tanaka, *J. Phys. Chem. C* 113 (2009) 18713–18718.
- [35] T. Shishido, K. Teramura, T. Tanaka, *Catal. Sci. Technol.* 1 (2011) 541–551.
- [36] S. Furukawa, Y. Ohno, T. Shishido, K. Teramura, T. Tanaka, *Shokubai* 53 (2011) 132–134.
- [37] S. Furukawa, Y. Ohno, T. Shishido, K. Teramura, T. Tanaka, *ChemPhysChem* 2011, doi:10.1002/cphc.201100388, in press.
- [38] R.G.W. Norrish, C.H. Bamford, *Nature* 138 (1936) 1016.
- [39] R.G.W. Norrish, C.H. Bamford, *Nature* 140 (1937) 195–196.
- [40] K. Ohkubo, K. Suga, S. Fukuzumi, *Chem. Commun.* 201 (2006) 8–2020.